HALOCARBON PRODUCTS CORPORATION - USE OF METHYLENE CHLORIDE AS HEAT TRANSFER FLUID OCCUPATIONAL EXPOSURE AND RISK ESTIMATES

EXPOSURE ESTIMATION

Methods:

All occupational exposures were estimated using EPA ChemSTEER v3.0 (version: 09/30/2013) using the physical-chemical data published in EPA's Final Risk Evaluation document and using the default model parameters unless otherwise noted. The specific models used and relevant user inputs are described in the subsections that follow.

Chemical Properties - The following chemical properties were used in the assessment:

Total Assessed Volume (Pv): 250 kg/yr Vapor Pressure (VPchem): 435 torr @ 25 °C Molecular Weight (MW): 84.93 g/mol Density (Dchem): 1.33 g/cm3 @ 20 °C

Solubility in Water (WSchem): 13 g/L @ 25 °C

The Pv = 250 kg/yr was chosen as a worst case and represents up to 50 maintenance activities per year on the system, each of which involves loss of < 1 gallon of methylene chloride. The entire system holds 2700 gallons (13,593 kg) and, in the past 30 years, has only ever had to be completely drained and replaced once, representing only 453 kg/yr.

<u>Operations</u> - Figure 1 shows a representation of the system. As indicated, operation of the system involves limited opportunities for exposure to methylene chloride, otherwise the system is completely closed. The only notable exposures are:

- [A1] transferring new methylene chloride into the charge tank
- [A2] sampling
- [A3] maintenance (e.g. pump seal failure)

Given the above activities, the following operations were assessed:

Unloading Liquid Raw Material from Drums
Sampling Liquid Raw Material (*) / (*) Includes maintenance (see discussion below)

Cleaning empty drums was not assessed as this activity is not performed at the site and is commonly associated with environmental release rather than worker exposure. Empty drums are sent offsite for recovery and/or disposal. With regards to [A3] maintenance, a typical activity would involve repairing a pump seal failure, in which case the site's written policies state that before a line break is permitted, the pump must first be cleared with nitrogen making sure to discharge the nitrogen and any methylene chloride vapor into the system (not to atmosphere). Then, any residual methylene chloride remaining in the pump/line is drained/collected in a container, similar to a sampling activity. Since these exposures involve maintenance personnel rather than operators who perform the sampling, the exposure assessments for sampling was used to represent a typical and worst-case maintenance activity as well. In other words, there was no need to double the amount of exposure to any individual worker.

Operation Parameters - The following operation parameters were used:

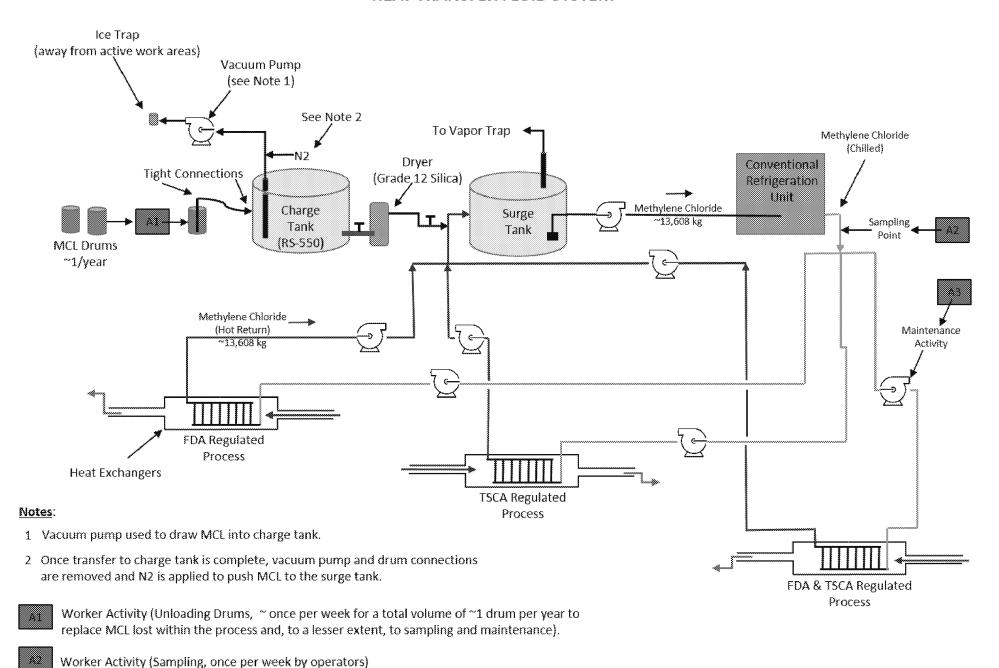
Type of Operation: Batch Operation (Using Raw Material)

Number of Sites (NS): 1

Total batches/site-year (Nby): 52

Weight fraction (Yrm): 1

FIGURE 1 – METHYLENE CHLORIDE (MCL) HEAT TRANSFER FLUID SYSTEM



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- Worker Activity (Maintenance, < once per week by maintenance personnel)

The Nby = 52 was chosen as the maximum number of days per year that a worker would be exposed to methylene chloride either as a result of a weekly sampling activity (operators) or a weekly maintenance activity (maintenance personnel), with the former representing the actual frequency and the latter representing a worst-case estimate of the frequency. This also corresponds to a worst-case frequency for unloading drums of MCL to replace the volume lost due to process leaks that are contained within the process and, to a lesser extent, the volume lost from sampling and maintenance activities.

<u>Models Used & Inputs</u> - The following ChemSTEER models and inputs were used to estimate chemical exposure:

Activity	Dermal Model(s)	Inhalation Model(s)	Non-Default Inputs
Unloading MCL from Drums	2-Hand Dermal Contact with Liquid Model	Mass Balance Model	- AT = 31 years (Typical) or 40 years (Worst Case) - ATc = 78 years - BW = 80 kg - EY = 31 years (Typical) or 40 years (Worst Case) - NWexp = 4 - G: 0.03847557 g/s (1) - Yderm = 0.08 (2)
Sampling MCL	1-Hand Dermal Contact with Liquid Model	Mass Balance Model	- AT = 31 years (Typical) or 40 years (Worst Case) - ATc = 78 years - BW = 80 kg - EY = 31 years (Typical) or 40 years (Worst Case) - NWexp = 4 - G = 0.1383893 g/s (1) - Yderm = 0.08 (2)

⁽²⁾ Per EPA/OPPT Mass Transfer Coefficient Model.

Exposure Estimate Results:

The following exposure estimates where generated from the ChemSTEER model:

Worker Inhalation Exposure to Methylene Chloride during Unloading Drums

	Central Tendency	Worst Case
Model Output / Model Result:		
Potential Dose Rate (mg/day)	7.2827 x 10 ⁻⁴	6.5544 x 10 ⁻³
Calculated from the Above Model Result / Values Used	for MOE Risk Calculations:	
8-hr TWA Exposure Concentration (mg/m³) (1)	7.2827 x 10 ⁻⁵	6.5544 x 10 ⁻⁴
Average Daily Concentration (ADC)(mg/m³) (2)	3.4585 x 10 ⁻⁶	3.1126 x 10 ⁻⁵
Lifetime Average Daily Concentration (LADC) (mg/m³) (3)	6.0204 x 10 ⁻⁶	6.9914 x 10 ⁻⁵

^{(1) 8-}hr TWA (mg/m³) = Potential Dose Rate (mg/day) x (8 hrs/day) $^{-1}$ x (1.25 m³/hr) $^{-1}$, where 1.25 m³/hr is respiration rate.

⁽³⁾ Yderm = Weight Fraction (Wf) x Proportion Remaining on Skin (fabs) = 1 x 0.08 = 0.08

⁽²⁾ ADC (mg/m³) = (8-hr TWA (mg/m³) x 8 hr/day x 250 days/yr x WY) ÷ (WY x 365 days/yr x 24 hr/day), where WY=31 or 40.

⁽³⁾ LADC (mg/m³) = (8-hr TWA (mg/m³) x 8 hr/day x 250 days/yr x WY) ÷ (78 x 250 days/yr x 24 hr/day), where WY=31 or 40.

Worker Inhalation Exposure to Methylene Chloride during Sampling

	Central Tendency	Worst Case				
Model Output / Model Result:						
Potential Dose Rate (mg/day)	3.017	27.1534				
Calculated from the Above Model Result / Values Used for MOE Risk Calculations:						
8-hr TWA Exposure Concentration (mg/m³) (1)	3.017 x 10 ⁻¹	2.7153				
8-hr TWA Exposure Concentration (mg/m³) (1) Average Daily Concentration (ADC)(mg/m³) (2)	3.017 x 10 ⁻¹ 1.4327 x 10 ⁻²	2.7153 1.2895 x 10 ⁻¹				

^{(1) 8-}hr TWA (mg/m³) = Potential Dose Rate (mg/day) x (8 hrs/day) 1 x (1.25 m³/hr) 1 , where 1.25 m³/hr is respiration rate.

Worker Dermal Exposure to Methylene Chloride during Unloading Drums

	Central Tendency	Worst Case				
Model Output / Model Results:						
Acute Potential Dose (mg/kg-day)	0.749	2.247				
Average Daily Dose (mg/kg-day)	0.1067	0.3201				
Lifetime Average Daily Dose (mg/kg-day)	0.042	0.1642				

Worker Dermal Exposure to Methylene Chloride during Sampling

Central Tendency Worst Case						
Model Output / Model Results:						
Potential Dose Rate (mg/kg-day)	0.3745	1.1235				
Average Daily Dose (mg/kg-day)	0.053	0.1601				
Lifetime Average Daily Dose (mg/kg-day)	0.021	0.082				

RISK CHARACTERIZATION

Given the exposure estimates above and using EPA's risk characterization methodology, the relevant MOEs and cancer risks are calculated as follows:

Risk Estimate for Acute, Non-Cancer Inhalation Exposures

HEC Time Period	Acute HEC	Exposure	MOEs for Acute Exposures			Benchmark
Endpoint = CNS Effects	(mg/m³)	Level	No Respirator	APF 25	APF 50	MOE
8-hr (Drum Unloading)	290	High-End	4.4245 x 10 ⁵	N/A	N/A	30
		Central Tendency	3.9820 x 10 ⁶	N/A	N/A	30
8-hr (Sampling)	200	High-End	1.0680 x 10 ²	N/A	N/A	20
	290	Central Tendency	9.6122 x 10 ²	N/A	N/A	30

Risk Estimate for Chronic, Non-Cancer Inhalation Exposures

Endpoint	Chronic HEC	Exposure	MOEs for Acute Exposures			Benchmark
(Activity)	(mg/m³)	Level	No Respirator	APF 25	APF 50	MOE
Liver Effects (Drum Unloading)	47.0	High-End	5.5259 x 10 ⁵	N/A	N/A	10
	17.2	Central Tendency	4.9733 x 10 ⁶	N/A	N/A	10

⁽²⁾ ADC (mg/m³) = (8-hr TWA (mg/m³) x 8 hr/day x 250 days/yr x WY) ÷ (WY x 365 days/yr x 24 hr/day), where WY=31 or 40.

⁽³⁾ LADC (mg/m³) = $(8-hr TWA (mg/m³) \times 8 hr/day \times 250 days/yr \times WY) \div (78 \times 250 days/yr \times 24 hr/day)$, where WY=31 or 40.

Endpoint	Chronic HEC	Exposure	MOEs for Acute Exposures			Benchmark
(Activity)	(mg/m³)	Level	No Respirator	APF 25	APF 50	MOE
Liver Effects (Sampling)	47.2	High-End	1.3339 x 10 ²	N/A	N/A	10
	17.2	Central Tendency	1.2005 x 10 ³	N/A	N/A	10

Risk Estimate for Chronic, Cancer Inhalation Exposures

Endpoint	IUR	Exposure	MOEs for Acute Exposures			Benchmark
(Activity)	(risk per mg/m³)	Level	No Respirator	APF 25	APF 50	MOE
Cancer Risk (Drum Unloading)	1.38 x 10 ⁻⁶	High-End	10-11	N/A	N/A	10 ⁻⁴
		Central Tendency	10 ⁻¹²	N/A	N/A	10
Cancer Risk (Sampling)	4.20 406	High-End	10 ⁻⁷	N/A	N/A	10-4
	1.38 x 10 ⁻⁶	Central Tendency	10-8	N/A	N/A	10 ⁻⁴

MOEs for Acute Dermal Exposure for CNS Effects POD = 16 mg/kg/day, Benchmark MOE=30

Activity	Exposure	MOEs with Glove PFs				
Activity	Level	No Gloves	PF 5	PF 10	PF 20	
Unloading Drums	High-End	7.12	35	N/A	N/A	
	Central Tendency	21.4	107	N/A	N/A	
Sampling	High-End	14.24	71.2	N/A	N/A	
	Central Tendency	42.7	N/A	N/A	N/A	

MOEs for Chronic Dermal Exposure for Liver Effects POD = 2.15 mg/kg/day, Benchmark MOE=10

Application	Exposure	MOEs with Glove PFs				
Activity	Level	No Gloves	PF 5	PF 10	PF 20	
Unloading Drums	High-End	6.7	33.5	N/A	N/A	
	Central Tendency	20.1	100	N/A	N/A	
Sampling	High-End	13.4	67	N/A	N/A	
	Central Tendency	40.6	N/A	N/A	N/A	

Cancer Risk for Chronic Dermal Exposure CSF = 1.1 x 10⁻⁵ per mg/kg/day

A astrologic	Exposure	MOEs with Glove PFs				
Activity	Level	No Gloves	PF 5	PF 10	PF 20	
Unloading Drums	High-End	10 ⁻⁶	N/A	N/A	N/A	
	Central Tendency	10 ⁻⁷	N/A	N/A	N/A	
Sampling	High-End	10 ⁻⁷	N/A	N/A	N/A	
	Central Tendency	10 ⁻⁷	N/A	N/A	N/A	

SUMMARY AND CONCLUSIONS

Given the conservative exposure and risk estimates outlined above, using EPA methodology, all MOEs exceed the applicable target MOEs and all cancer risks are less than 10^{-4} , with and without regards to the use of respiratory protection. Regarding dermal exposures, exposure estimates suggest a potential for significant acute and chronic exposure, for non-cancer effects only, without the use of gloves during drum unloading and sampling activities. However, the assessment further shows that dermal exposure can be adequately controlled by the use of even the least protective gloves when direct contact to methylene chloride is possible.